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ARMOUR RESEARCH FOUNDATION OF ILLINOIS INSTITUTE OF TECHNOLOGY

TECHNOLOGY CENTER

ARF Project D217

Contract No. DA-18-108-405-CML-777

INHIBITION OF FLASHING OF AEROSOLS

Quarterly Progress Report VI

G. G. M...

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Armour Research Foundation of
Illinois Institute of Technology, Chicago, Illinois

INHIBITION OF FLASHING OF AEROSOLS - C.C. Miesse

Qtrly Report No. VI, 15 November 1961, 15 pp - 3 illus.
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This report covers the period from July 15, 1961 to October 14, 1961, during which the lower flammability limit curve for dibutyl phthalate (DBP) was determined for mass median drop diameters (MMD) from 8 to 365 microns, and the inhibitive effect of 0.7 per cent (by volume) of gaseous bromotrifluoromethane (Freon 13B-1) was noted.

Flammability tests using the large drop aerosol generator indicated an increase in lower limit flammability concentrations for mass median diameters above 200 microns, so that the curve attains a minimum value in the 100 - 200 micron MMD range. Addition of 0.7 per cent CF_3Br

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Experimental techniques were perfected for nuclei generation necessary for small drop aerosols, and determination of the impression factor for large drop DBP aerosols.

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ILLINOIS INSTITUTE OF TECHNOLOGY

DA-18-108-405-CML-777

Quarterly Progress Report No. VI

July 15, 1961 to October 14, 1961

INHIBITION OF FLASHING OF AEROSOLS

C. C. Miesse

November 15, 1961

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The sixth Quarterly Progress Report summarizes the work performed during the past quarter, from July 15, 1961 to October 14, 1961, under Contract No. DA-18-108-405-CML-777, on the study of "Inhibition of Flashing of Aerosols", for the Physical Chemistry Division of the Army Chemical Center, Edgewood, Maryland.

The following personnel have contributed to this project during the sixth quarter: C. C. Miesse and D. K. Werle.

Data are recorded in Armour Research Foundation Logbooks C-10313 and C-11642.

Respectfully submitted,

ARMOUR RESEARCH FOUNDATION OF
ILLINOIS INSTITUTE OF TECHNOLOGY

C C Miesse

C. C. Miesse, Principal Investigator

APPROVED:

T. H. Schiffman

T. H. Schiffman, Assistant Director of
Fluid Dynamics and Propulsion Research

CCM/aa

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INHIBITION OF FLASHING OF AEROSOLS

I. ABSTRACT

This report covers the period from July 15, 1961 to October 14, 1961, during which the lower flammability limit curve for dibutyl phthalate (DBP) was determined for mass median drop diameters (MMD) from 8 to 365 microns, and the inhibitive effect of 0.7 per cent (by volume) of gaseous bromotrifluoromethane (Freon 13B-1) was noted.

Flammability tests using the large drop aerosol generator indicated an increase in lower limit flammability concentrations for mass median diameters above 200 microns, so that the curve attains a minimum value in the 100 - 200 micron MMD range. Addition of 0.7 per cent CF_3Br to the air stream entering the lower end of the combustion tube increased the lower flammability limit from 18.6 to 42.5 mg/liter for DBP aerosols with an MMD of 205 microns.

Experimental techniques were perfected for nuclei generation necessary for small drop aerosols, and determination of the impression factor for large drop DBP aerosols.

II. INTRODUCTION

This project under Contract DA-18-108-405-CML-777 was initiated on April 15, 1960, by the Army Chemical Center, to investigate fundamental behavior in the flashing of flammable liquid aerosols so that means of prevention or inhibition of the flashing may be revealed. The variables to be investigated include mass concentration, drop size, liquid volatility, ignition source, and, if possible, pressure and temperature. In the second phase of this study, flame inhibiting additives will be investigated.

During the sixth quarter, the variation of lower limit flammability concentration for DBP aerosols was determined over the MMD range of 8 to 365 microns and the inhibitive effect of bromotrifluoromethane added to the primary air supply was noted. Minimum flammability concentrations were found to decrease with drop size for MMD less than 150 microns, and then increase again for larger drop aerosols. This type of variation tends to support the hypothesis of vapor phase combustion, since the predominance of diffusion over evaporation rate in the smaller drops (due to smaller distances between drops in a consist of given liquid concentration) tends to result in a more homogeneous gaseous mixture at a relatively low concentration, while the slower over-all mass evaporation rate in the large drop aerosols provides a weaker source of flammable vapors.

III. EXPERIMENTAL TECHNIQUES

In order to examine the variation of lower-limit flammability concentrations with the MMD of the aerosols, it was necessary to develop techniques for producing very small-drop aerosols in flammable concentration, and for determining the impression factor (drop diameter to collecting slide impression diameter ratio) for large drops.

A. Nuclei Generator for Small-Drop Aerosols

As shown in Fig. 1, a nuclei generator incorporating a 3500 volt discharge across gold electrodes was used to produce a DBP aerosol with drops of the order of 10 microns in diameter. The low settling velocity of these droplets precluded purging of the carrier nitrogen gas by a rising air column in the combustion tube. Therefore, oxygen was

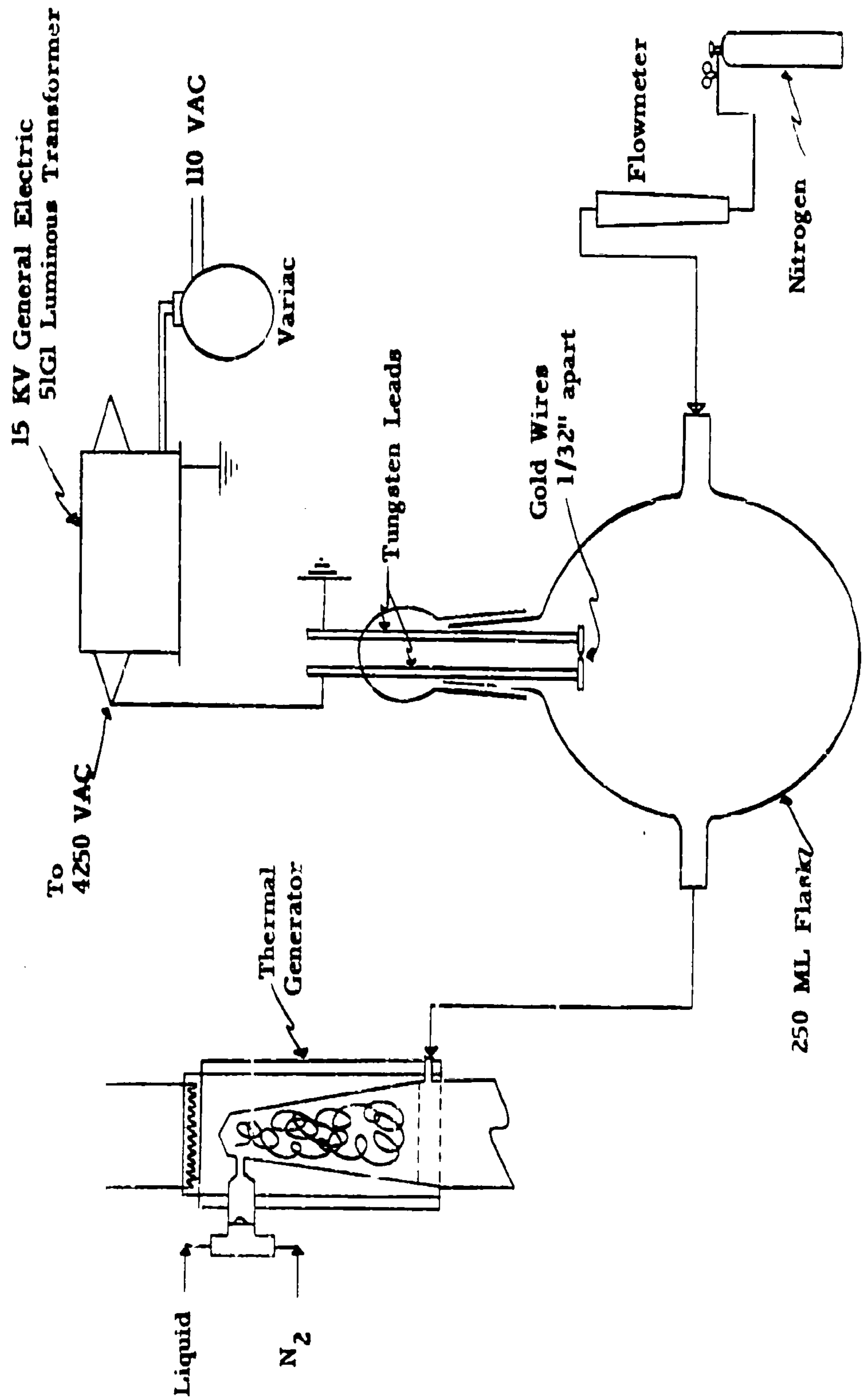


Fig.1 NUCLEI GENERATOR

metered into the aerosol below the condenser tube such that 21 per cent oxygen was present in the combustion tube. Upon ignition, the flame front appeared continuous. As the flame proceeded up the combustion tube it appeared to accelerate and was accompanied by a loud roaring sound which increased in intensity. In previous tests with the larger drops the discontinuous flame front proceeded in a fairly uniform manner up the combustion tube and little combustion noise was noticed. As shown in Table I, the lean limit for the 10 micron DBP aerosols was much higher than that for the 35 - to - 120 micron DBP aerosols.

B. Variations of Impression Factor with Drop Size

Since the accuracy of the slide techniques for determining aerosol drop size distributions is dependent upon a precise knowledge of the ratio of drop-to-impression diameters, it was essential that this magnesium-oxide impression factor be determined for large drops, for which no previous data have been reported. The value of 0.86 determined by May (1) was used for the 20- to 200 micron drops, but May's work did not cover the drops over 200 microns in size. Since a uniform aerosol is required for this purpose, a vibrating capillary drop generator (2) was constructed and the impression factor was determined by gravimetric measurements: several drops collected on a coated slide were weighed and an average drop diameter was calculated and compared with the impression size observed in the microscope. It is evident that the impression factors listed in Table I decrease with increasing drop size for drop sizes greater than 200 microns.

Table I

Drop Size, microns	Impression Factor
150	0.87
200	0.87
300	0.86
400	0.84
500	0.80
600	0.74
700	0.67
800	0.63
1000	0.59
1500	0.51

IV. FLAMMABILITY LIMITS

Perfection of the techniques for producing DBP aerosols in the 10 and 300 micron (MMD) ranges has permitted extension of the lower flammability limit curve at both ends, such that minimum concentration for flame propagation has now been determined for aerosols with MMD's ranging from 8 to 365 microns. The results are summarized in Table II and Fig. 2, which indicates that larger concentrations are required for both extremely small and relatively large drop size aerosols, resulting in a U-shaped curve. The high concentrations necessary for flame propagation of fine-drop aerosols corresponds closely with the data presented by Burgoyne and Cohen (3) for tetralin aerosols, but the behavior of the curve for large drop aerosols has not been noted in the literature.

A plausible explanation of the apparent requirement for large concentrations at both the fine-drop and large-drop ends of the curve

Table II
LEAN LIMIT DATA FOR DBP AEROSOLS

Test No.	Diameter, microns Arithmetic Mean	MMD	Lean Limits, mg/l
1	62	93	26.7
2	82	109	27.8
3	99	150	27.1
4	95	114	24.9
5	66	99	22.9
6	66	98	21.2
7	118	135	17.3
8	119	133	18.5
9	117	129	18.2
10	35	84	28.6
11	34	69	27.1
12	41	79	27.5
13	7.8	8.6	68.3
14	7.7	8.5	67.0
15	7.8	8.6	67.3
16	143	205	42.4 *
17	288	346	42.5
18	271	365	43.4

* Concentration used in gaseous inhibitor tests, Table I

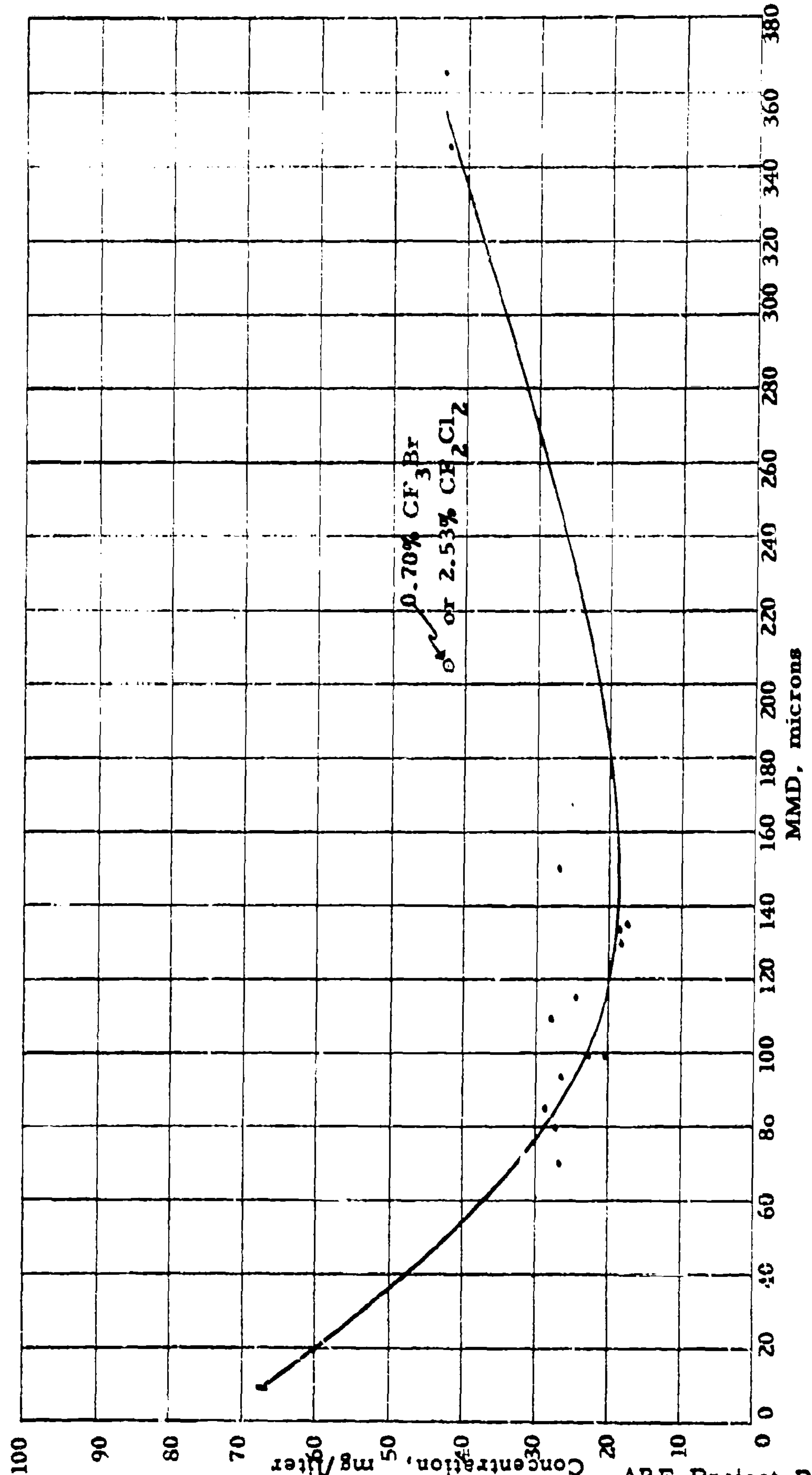


Fig. 3 VARIATION OF LEAN LIMIT OF DBP VERSUS MMD

is derived from observation of the striking difference in the two respective flame appearances shown in Fig. 3. The small-drop aerosol (3a) is seen to burn with a single large-scale luminous flame, characteristic of the combustion of gaseous mixtures, as noted previously by Browning and Krall (4) as well as Burgoyne and Cohen (3). The large-drop aerosol (3b) however exhibits a distinctively different drop-to-drop combustion pattern, indicating that the flame propagates from one region of flammable concentration to the next, greater luminosity resulting from fuel-rich regions adjacent to the large drops.

Theoretical analysis of the U-curve phenomenon involves consideration of the dimensionless parameter $b/s_f = M/4\pi\rho\alpha s_f = \rho'\lambda/8\rho\alpha$ (5) presented in Quarterly Progress Report No. II, where

M = mass evaporation rate, gm/sec

s_f = radius of droplet, cm

α = diffusion rate, cm^2/sec

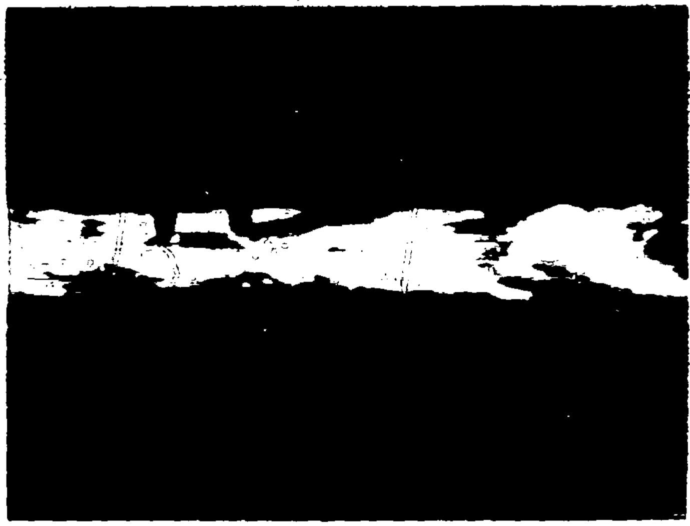
λ = surface evaporation rate, cm^2/sec

ρ = density of vapor, gm/cm^3

ρ' = density of liquid, gm/cm^3

For equal liquid concentrations, it is apparent that the spacing of smaller drops must be much smaller than for larger drops. Hence, the distance between them must be much less, such that diffusion will lead more rapidly to a relatively homogeneous gaseous mixture. Since the vapors are thus spread over the entire volume, the over-all vapor concentration will be less than that found in the regions adjacent to the larger drops, thus requiring a greater liquid concentration to provide a flammable

a. MMD = 8 microns



b. MMD = 120 microns

Fig. 3 TYPICAL AEROSOL FLAME CONFIGURATION (OPEN SHUTTER EXPOSURE) vapor concentration. Flame propagation for small drop aerosols, can therefore be described as a diffusion-controlled process, since the smaller distances associated with fine drop aerosols leads to more rapid development of a homogeneous gaseous mixture.

For large drop aerosols, on the other hand, it appears that vaporization rate (M) is the controlling factor. The total mass evaporation rate M_T can be represented by

$$M_T = N\,M = N\,k\,s_f \qquad (1)$$

where N is the number of droplets and k is a proportionality factor. For a given liquid concentration C, the number of droplets varies inversely as the cube of the radius s_f:

$$N = 3\bar{C}/4\,\pi\,\rho'\,(s_f)^3 \qquad (2)$$

From Equations 1 and 2, it is obvious that the total mass rate of vapor formation varies inversely as the square of the droplet radius

$$M_T = 3\bar{C}\,k/4\,\pi\,\rho'\,(s_f)^2 \qquad (3)$$

so that if a minimum over-all vapor concentration is required for flame propagation, it is apparent that increased liquid concentrations are required for larger droplets.

V. INHIBITION BY GASEOUS ADDITIVE

In the initial inhibitor tests, the gaseous inhibitor was premixed with air before passage into the bottom of the combustion tube. An excess amount of the inhibitor-containing air was supplied to the combustion tube inlet, and the excess issued from an adjacent 5/8-inch opening . Ignition could be effected either by shorting a 3/4-inch length of No. 30 B and S nichrome wire, or by insertion of the pilot gas igniter. The thermal generator was adjusted to produce a 205 micron MMD aerosol at 42.4 mg/liter, and the inhibitor concentration was gradually increased until complete suppression was achieved. The data are presented in Table III, and the great increase in DBP concentration required for flame propagation is shown in Fig. 3.

Table III

GASEOUS INHIBITOR EFFECTS ON A DBP AEROSOL

Inhibitor	% Concentration	Effect
CF_3Br	0.35 - 0.70	Will not propagate if pilot igniter is withdrawn
(Freon 13B-1)	0.70 - 1.62	Will not propagate when pilot igniter is left in tube
	over 1.62	Will not propagate, will not ignite
CF_2Cl_2	1.42 - 2.53	Will not propagate if pilot igniter is withdrawn
(Freon 12)	2.53 - 3.38	Will not propagate when pilot igniter is left in tube
	over 3.38	Will not propagate, will not ignite

Three inhibitor concentration ranges were observed for each inhibitor. In the lower range it was noted that upward propagation took place only when pilot igniter was left in the combustion tube after insertion. Rapid withdrawal of the igniter resulted in a small burst of ignition which failed to propagate more than several inches. In the intermediate range of inhibitor concentration, propagation failed to occur even when the igniter was left in the combustion tube, although ignition did take place. In the upper range of inhibitor concentration, ignition by either the gas pilot igniter or the shorted wire was completely suppressed; the pilot flame itself was extinguished at this concentration. These extinguishing concentrations correspond closely with the values reported for natural gas diffusion flames by E. C. Creitz (6), who noted that introduction of the inhibitor into the oxidizing stream was infinitely more effective than premixing of the additive with the natural gas.

VI. CONCLUSIONS

As a result of the experimental investigation carried out during the preceding quarter, the following conclusions can be drawn, relative to DBP aerosols:

1. "Mechanical" inhibition of flammability is encountered for aerosols in the very low ($<$ 10 microns MMD) or very high ($>$ 300 microns MMD) drop-size regimes. Hence, the incidence of flammability can be minimized by developing a dispersion technique which produces aerosols in either of these extreme drop-size ranges.

2. Chemical inhibition of flammability is effected by the mixing of less than one per cent (by volume) of bromotrifluoromethane (CF_3Br) with the ambient air supply. Such a technique, although not feasible in field operations, may well be achieved by addition of a rapidly vaporizing chemical to the aerosol-producing liquid.

VII. SPONSOR VISIT

On the occasion of his visit to the Armour Research Foundation on 13 October 1961, J. Goldensen, Chief of the Colloid Branch, made the following recommendations:

1. Investigate the effect of liquid volatility on the flashing phenomenon by subjecting a series of similar compounds (e.g., phthalates or phosphates) to experimental evaluation.
2. Determine the variation of flame speed with respect to both simulant and mass median diameter of the aerosol.
3. Determine the spontaneous ignition temperatures for each simulant investigated.
4. Include more detailed explanation of trends observed and applicability of the results to the flashing problem, in future reports.

VIII. TECHNICAL PRESENTATION

As a result of the present investigation, the following technical report has been prepared for presentation at the AIChE Symposium on Spray Phenomena (4 February 1962 in Los Angeles) and was submitted for approval by the Directorate of Research: "Vapor Concentration in a Thermally-Generated Aerosol".

IX. FUTURE WORK

The research program for the period from 15 October 1961 to 14 January 1962 will include the following investigations:

1. Determination of the effect of volatility on flammability by experimentation with a series of similar compounds.
   a. Variation of lean limit flammability concentration with MMD
   b. Flame propagation rates

c. Spontaneous ignition temperature

2. Determination of the effect of several gaseous inhibitors on flammability and spontaneous ignition temperatures of the several compounds.

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